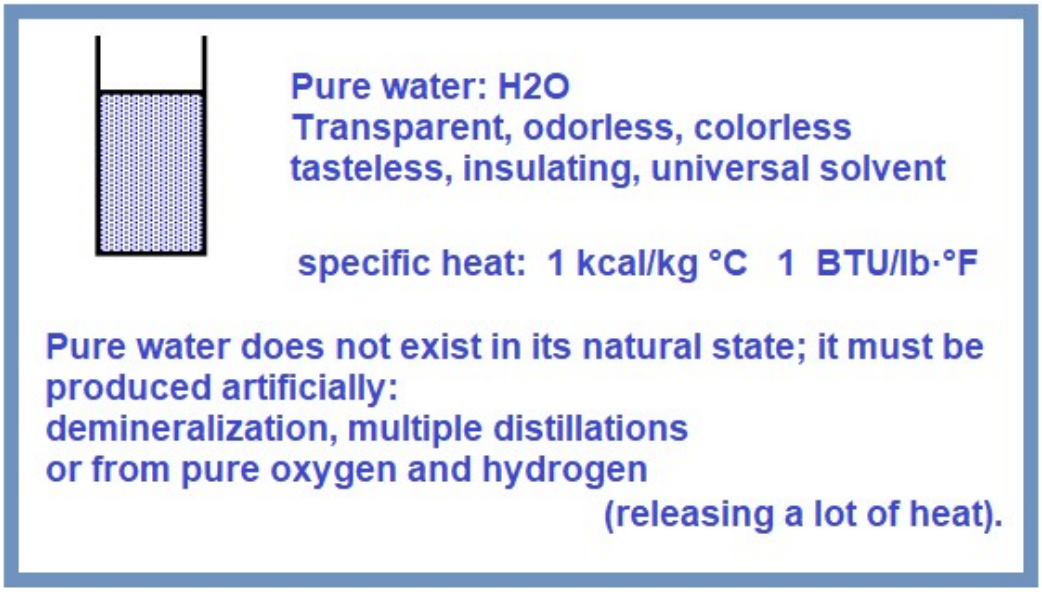
CHAPTER 2 Part 2: The water

THE WATER

We have seen that water is composed of a molecule made up of two hydrogen atoms and one oxygen atom. This water can be found in solid (ice), liquid (water), or gaseous (vapor) form. In our case, we will discuss water in its liquid and vapor forms.


Pure water: H2O
Transparent, odorless, colorless
tasteless, insulating, universal solvent
specific heat: 1 kcal/kg °C 1 BTU/lb·°F
Pure water does not exist in its natural state; it must be produced artificially:
demineralization, multiple distillations
or from pure oxygen and hydrogen
(releasing a lot of heat).

1- **Dissolved substances** that are either invisible or visible (due to color), and may or may not impart taste or odor.

(For example, table salt—sodium chloride—only imparts taste).

We will call these **Dissolved Salts sor Solids (T.D.S.)** because their molecules "mix" with those of water. These salts are measured in different ways to determine their quantity and identify them.

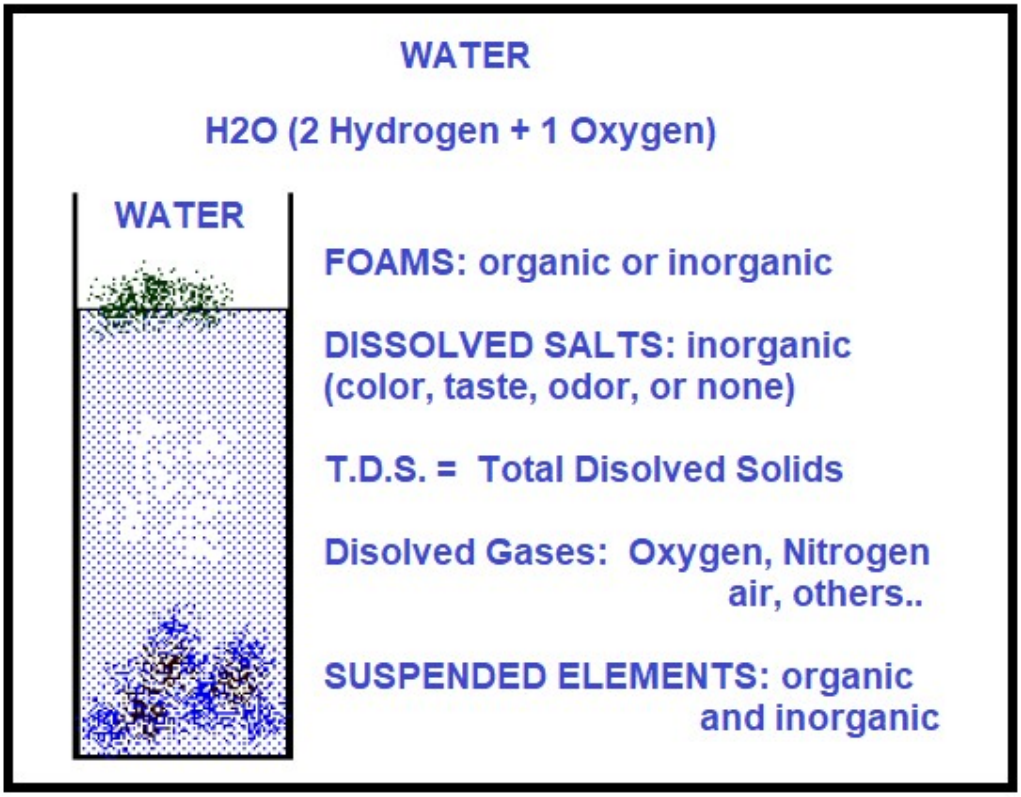
2- **Suspended solids** are materials that do not fully dissolve in water. Their molecules remain bonded, forming small bodies (or clumps) that are generally visible and often affect the color, odor, and taste of the water. (These solids generally include microorganisms that live in or contaminate the water.)

3- **Dissolved gases**, like dissolved salts, are integrated with water molecules, but their state is generally very unstable, as they depend heavily on the water temperature and the partial pressure of the gas at the surface. (They may impart taste, odor, and color, or none at all.)

Water for human use must be purified, both of microorganisms (which cause diseases) and of those elements that cause taste, odor, and color (generally, all of these are part of the suspended solids).

Water containing excessive dissolved salts or that are harmful to human health (toxic substances such as nitrites, chromates, pesticides, etc.) must also be treated to reduce or completely eliminate these salts.

Therefore, we can say:



(*) Organic compounds are primarily based on the carbon atom, and are the fundamental building blocks of life.

(**) While inorganic compounds can be formed from any other element on the periodic table, although they sometimes also contain carbon. Inorganics are found in minerals, salts, water, and gases such as carbon dioxide.

Rainwater:

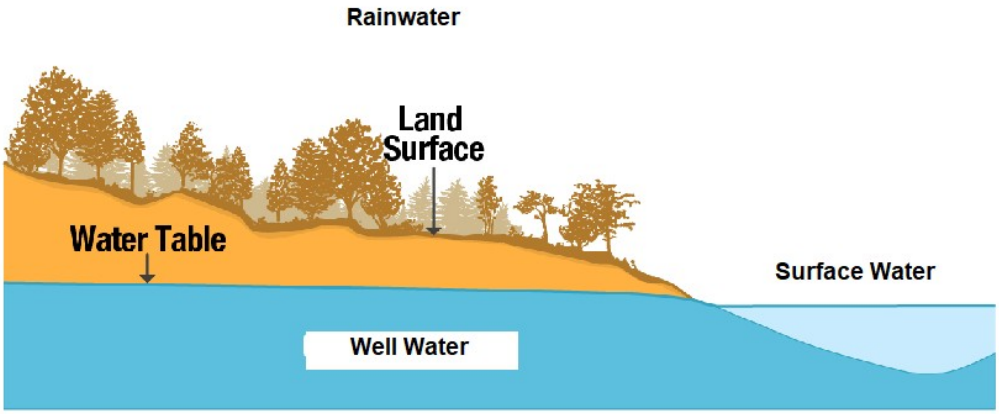
Very few dissolved salts, many gases (air, carbon dioxide, etc.), some suspensions (dust from the atmosphere and its microorganisms).

Surface water:

(rivers and lakes): Relatively few dissolved salts, quite a few gases and suspended materials (biological growth: microorganisms and agricultural products).

Well or Ground water:

Generally rich in dissolved salts, few gases, and low suspended solids content (almost none, except for sediment).



For human use, bacteriological purity is fundamental, as are chemical limits. It must be clean, without odors or tastes (nitrite being one of the elements harmful to human health, especially to young children).

Water for boilers must fundamentally meet the chemical requirements.

Let's see why:

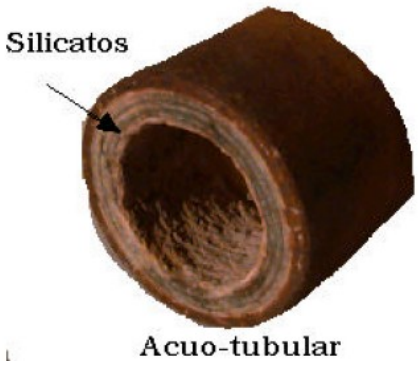
The water inside the boiler, due to its supply conditions and transformations caused by the increase in temperature or the increase in the concentration of its dissolved salts or suspended solids (due to evaporation inside the boiler, which leaves the salts and solids in the boiler water and the steam that comes out is "almost pure"), produces the following issues:

1-SCALES

this refers to the formation of a layer of "chemical" material that adheres to the walls of the heating surfaces, causing difficulties in the transmission of heat from the "fire" to the water, resulting in the metal overheating because the water does not "cool" it sufficiently – allowing the metal to "burn").

These scale deposits are generally formed by calcium and magnesium salts (two very common chemical elements in water – forming what we call "water hardness"). They commonly occur in water as dissolved salts in the form of highly soluble calcium and magnesium bicarbonates, decomposing inside the boiler into less soluble salts: highly insoluble calcium and magnesium carbonates, or their hydroxides, which are somewhat soluble.

Calcium carbonate (found in marble) can also contain magnesium carbonate, thus forming dolomite.



"Limescale" is calcium hydroxide and is partially soluble.

Due to heat and the chemical conditions of the water, magnesium bicarbonates tend to form magnesium hydroxide, a more scaling agent, forming "sludge" rather than direct scale, as its concentration increases.

Water can also contain other calcium and magnesium salts—of varying solubility—(generally sulfates and sometimes chlorides).

Sulfates often result from the water treatment process itself in urban water purification plants (in cities: when aluminum sulfate is used as a clarifying agent, it reacts with the water's natural alkalinity: calcium and magnesium bicarbonates).

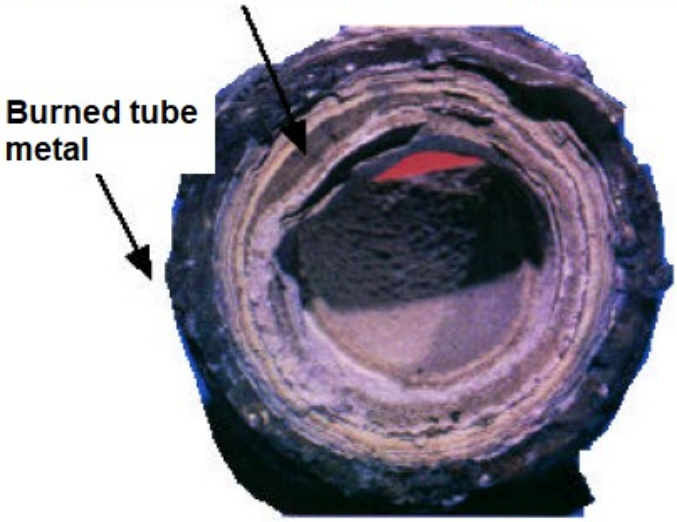
These sulfate scale deposits are extremely hard and difficult to remove. Sulfate scale is caused by an increase in its concentration inside the boiler, and because with increasing temperature it tends to precipitate, that is, to form a crystal that deposits on the hottest surface.

Silica (SiO2, or silicates, compounds that are present in water as salts or as a colloidal suspension) tends to form very hard scale deposits when it accumulates in boiler water.

Silica scale has a glassy or "sand", very hard and very difficult to extract mechanically and chemically, extremely insulating, not allowing heat to pass through to the water, even in small thicknesses.

Other times, the scale itself is "manufactured" by poorly done internal chemical treatments (generally due to the improper use of phosphates, polymers and purges, making these scales difficult to remove).

Example of different layers of scale according to stages of poorly performed chemical treatment

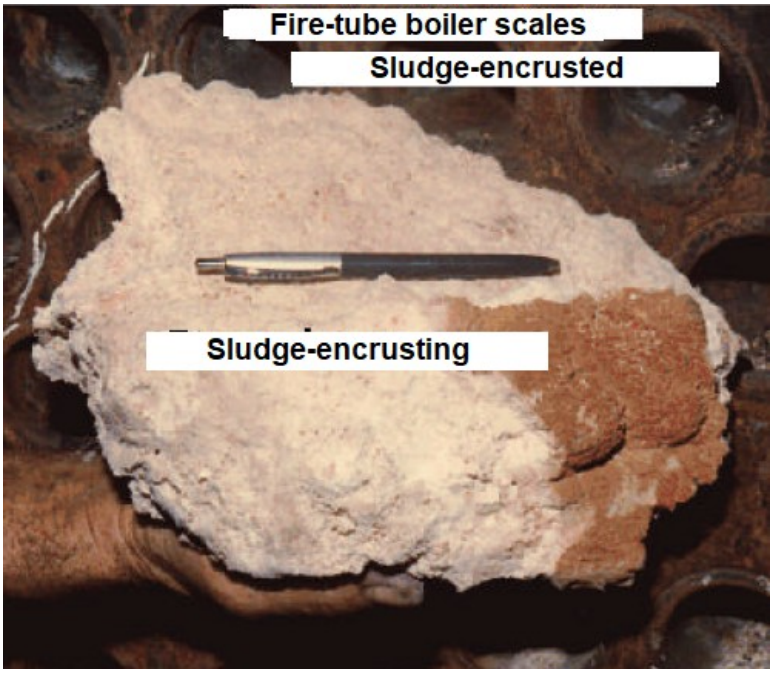


2-SLUDGES

We will define sludge as those salts that, once they precipitate, tend to agglomerate, forming suspended solids that, when combined, tend to deposit on heating surfaces or "bottoms," from which they cannot be removed by bottom purgue.

This sludge is formed by salts (of the type described above) and suspended solids that may come with makeup water or condensate, and from inadequate or nonexistent chemical water treatment.

The internal circulation of the boiler water plays a fundamental role in how this sludge can deposit and cause blockages to the cooling of the boiler metal. In fire-tube boilers without a cylindrical furnace (such as some recovery boilers or direct-fired wood boilers), the internal circulation between the tubes is upward, and a true "washout" of the tubes does not occur, allowing sludge to deposit on the tubes.



This does not happen when there is a cylindrical furnace. The cylindrical furnace (which acts as a circulation pump, washing the tubes) is one component. The other is the water-tube section of the boiler (especially in combustion chambers and flue gas return), where the sludge (which tends to descend due to gravity) is "pushed" upwards by the water circulation (which causes the sludge

to penetrate the tubes and allows its removal through the purge valves).

These tubes are generally ascending with a slight incline (especially in water-cooled grates or older "sectional" boilers).

Cleaning and periodic washing of the boiler are essential; that is, a semi-annual or at least annual hose cleaning, from top to bottom with a high flow of water.

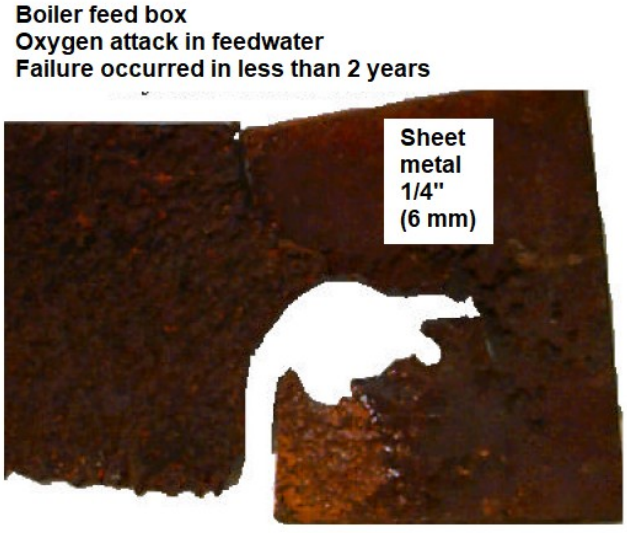
3- CORROSION

We will refer to corrosion as the attack on the metals of the boiler or system—steam and condensate lines, including equipment—causing pitting (perforations), generalized corrosion (attack on an entire area with metal loss, etc.).

The oxygen present in the water is the main cause and accelerator of corrosion processes in general.

We have exclusively chemical corrosions, but they are generally associated with electrochemical phenomena (temperature differences, dissimilar metals, stresses, pH, dissolved salts, oxygen, etc.).

It should be considered that corrosion is often caused by process products from the plant itself, or by products used in the treatment of the plant's drinking water, such as chlorine (which is generally used as sodium hypochlorite for water disinfection).



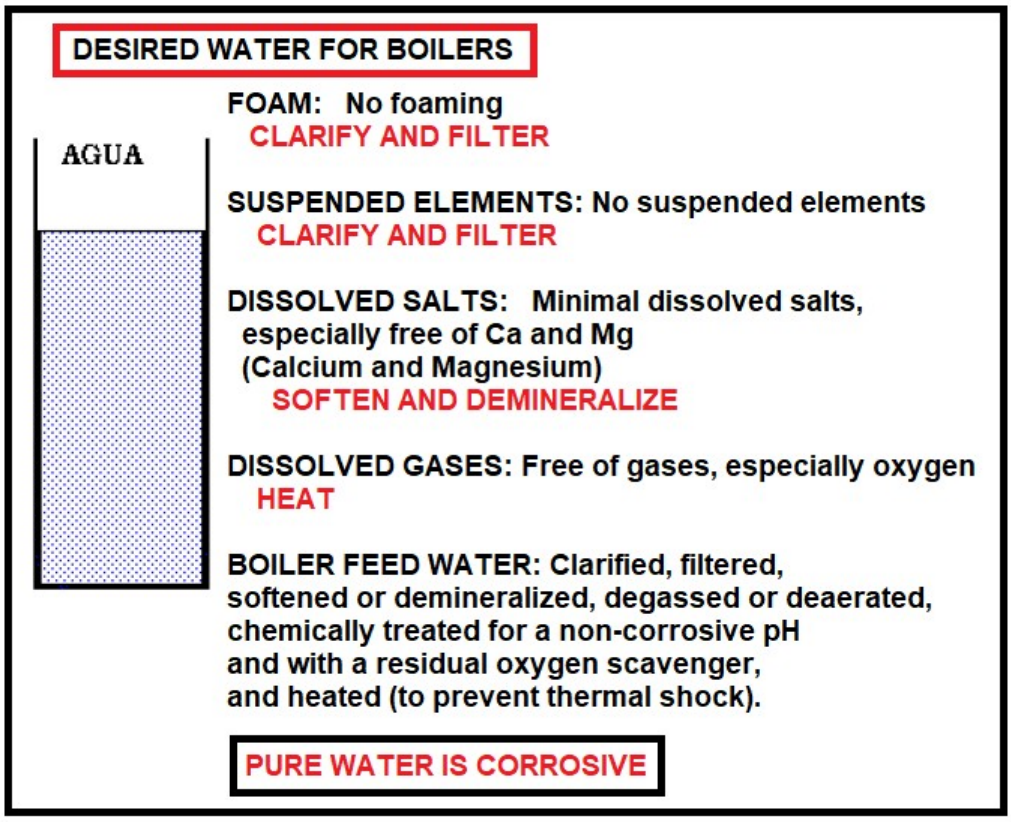
Chlorine is highly corrosive.

Unlike oxygen, chlorine can attack the boiler in any area (whether the boiler is running or stopped).

Removing chlorine from the makeup water is essential (although it can be chemically removed with sulfites, it is better to avoid using water that has had its chlorine removed by means of activated carbon filters).

Generally, oxygen attack occurs in boilers when they are stopped (manifesting as "pitting," or small perforations), usually in the steam tubes. However, as we will see below, in the boiler's water inlet system, when oxygen is released by heat and areas with different oxygen concentrations form, significant corrosion occurs (this is called "differential oxygen corrosion").

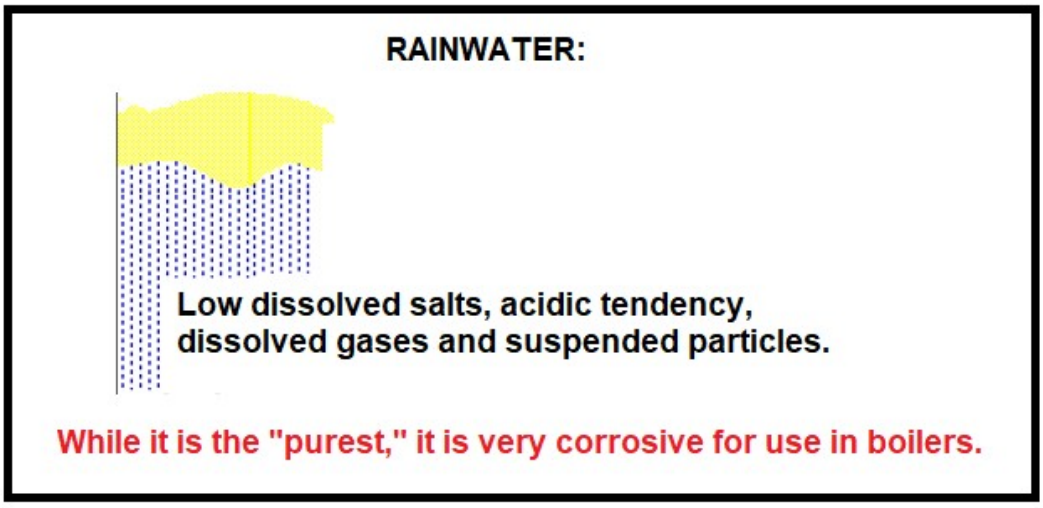
From the preparation of the water taken from a river (or a well, or distribution network, etc.) it must be treated as needed, since the problem of water is the whole "cycle" until its return as steam "condensate" when it returns to the feed tank.


DESIRED WATER FOR BOILERS
AGUA
FOAM: No foaming
CLARIFY AND FILTER
SUSPENDED ELEMENTS: No suspended elements
CLARIFY AND FILTER
DISSOLVED SALTS: Minimal dissolved salts, especially free of Ca and Mg (Calcium and Magnesium)
SOFTEN AND DEMINERALIZE
DISSOLVED GASES: Free of gases, especially oxygen
HEAT
BOILER FEED WATER: Clarified, filtered, softened or demineralized, degassed or deaerated, chemically treated for a non-corrosive pH and with a residual oxygen scavenger, and heated (to prevent thermal shock).
PURE WATER IS CORROSIVE

Methods for preparing different types of water for use:

The preparation of water for use depends on the type of boiler, operating pressure, and required steam quality.

Given the breadth of the topic, we will address the case of low-pressure boilers in general.


RAINWATER:
Low dissolved salts, acidic tendency,
dissolved gases and suspended particles.
While it is the "purest," it is very corrosive for use in boilers.

RAIN WATER:

This water is rarely used. It has the advantage of containing almost no salts (very few), but the high oxygen and carbon dioxide content of the air makes it highly corrosive. (In other cases, the salts present in the water form a protective "layer" or shield against corrosion; in this case, it doesn't form, making treatment necessary.)

To determine if water has a corrosive or scale-forming tendency, an analysis is performed using tables such as the Langelier Index, Ryznar Index, and Puckorius Index.

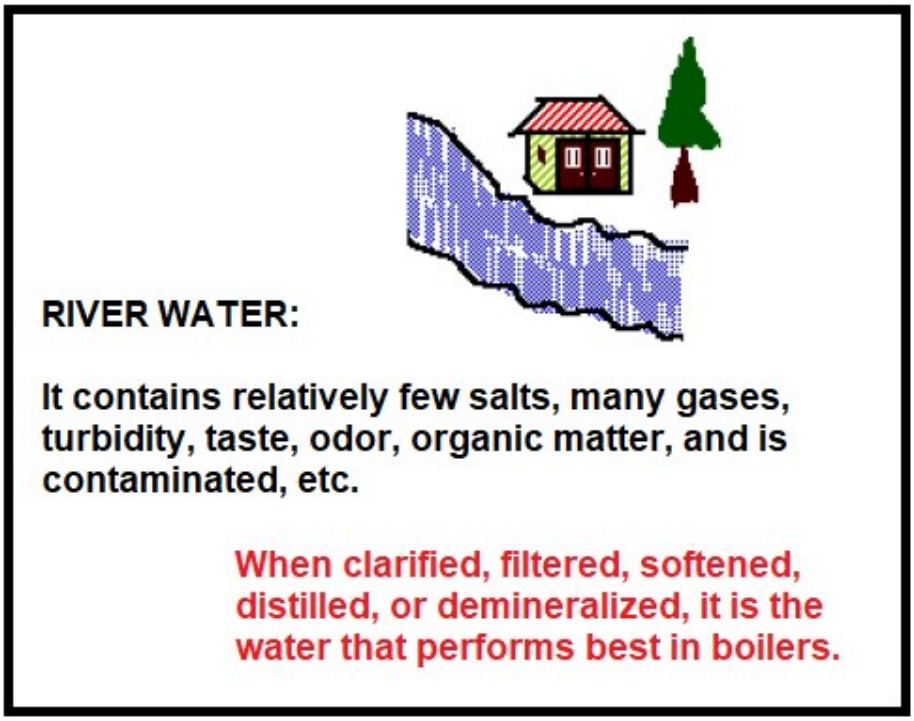
When treating rainwater for use in a boiler, it is essential to eliminate these gases (O2 and CO2). This can be achieved, firstly, by thoroughly heating the feedwater (or using a thermo-mechanical deaerator).

The solubility of gases in water is inversely proportional to temperature; that is, the higher the temperature, the less gas water can dissolve (we see this when opening a hot and a cold carbonated beverage; the hot one tends to overflow as the gas escapes quickly).

The residual oxygen must then be chemically removed (using sulfites, hydrazine, etc. - we must be very careful with the use of hydrazine because it is considered a "hazardous" substance).

The use of some of these chemical salts increases the salts inside the boiler, so the purge rate must be increased (sulfites).

Nowadays, rainwater is generally contaminated by environmental pollution, from chimney flue gases, but primarily by the large quantity of gases produced by the combustion of internal combustion engines, whether diesel or gasoline, both of which produce corrosive substances. But especially the gases from those who burn heavy fuel oil (which contains a large amount of sulfur).


RIVER WATER:
It contains relatively few salts, many gases, turbidity, taste, odor, organic matter, and is contaminated, etc.
When clarified, filtered, softened, distilled, or demineralized, it is the water that performs best in boilers.

RIVER WATER:

River water is the most common type of water used in boilers, as it is the water normally supplied by the state in Uruguay (treated by OSE).

These waters vary according to the time of year (evaporation) and rainfall, and have a high gas content (air, carbon dioxide, ammonia, etc.) due to being surface water.

The salt content is variable, but generally lower than in well water (which is why surface water is preferable to well water for boiler use; it requires less chemical treatment, less purge, etc.).

The "raw" river water must be treated (see the previous diagram): A product is added to the river water to remove suspended solids (generally aluminum sulfate, which reacts with the water's natural alkalinity: usually calcium and magnesium bicarbonates) in a mixer.

This causes the particles (along with microorganisms) to coagulate (neutralize the electrical charges that keep the suspended substances separate) and flocculate (clump together into a small sphere that tends to settle at the bottom of a container) so that they settle in a settling system (forming sludge).

From there, it is filtered (removing suspended materials that have not settled) and is also treated with a disinfectant (usually sodium hypochlorite) to eliminate any remaining microorganisms.

The pH is adjusted to prevent corrosion in the supply lines (soda ash or calcium hydroxide is added: slaked lime or quicklime; this replenishes the alkalinity that was consumed by the aluminum sulfate).

As we can see, these waters have only had suspended solids, odors, tastes, and microorganisms removed; the dissolved salt content has been increased, and the dissolved gases (oxygen, carbon dioxide, etc.) remain.

For use in boilers, we must remove scale-forming salts (those containing calcium and magnesium) or all salts (in the case of medium- and high-pressure boilers) and corrosive gases.

We can remove the calcium and magnesium salts that cause water hardness (or all salts) before using the water in the boiler or inside

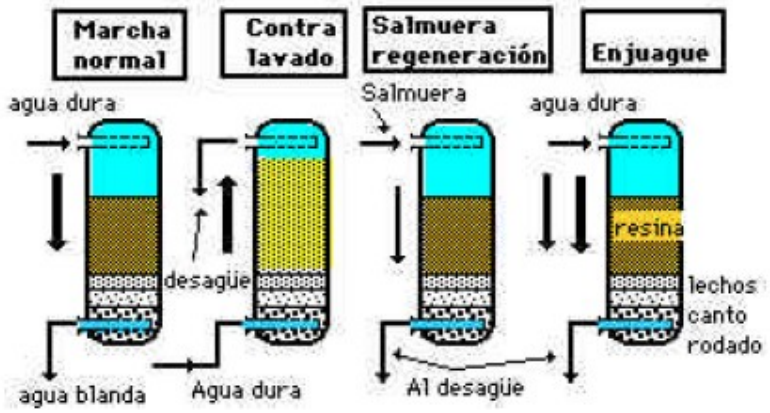
the boiler by transforming them into sludge that we can remove through the drains.

The most common method (in low-pressure boilers) to remove hardness before using the water is to use an ion exchanger (also called a water softener).

This device exchanges calcium and magnesium ions for sodium ions (small spheres charged with sodium take the calcium and magnesium ions and release a sodium ion as the water passes between them).

Once these spheres have depleted their sodium, they must be regenerated with sodium chloride (common salt).

When using a sodium-type ion exchanger (water softener), the total amount of salts remains the same because one type has been displaced by another. This water does not form scale but is highly corrosive because there is no salt to form a "protective" layer against the metal wall (scale, a stable oxide layer).



We can say that a water softener reduces the cost of treatment and keeps the boiler free of sludge. It is the first step in boiler water treatment (we will see others later); generally, the second step is internal chemical treatment.

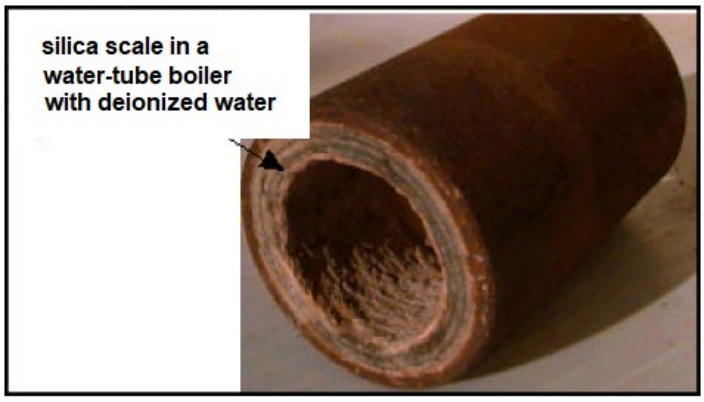
In the past, a large portion of the salts were removed through chemical precipitation (the salts reacted with other salts that were introduced, forming salts that precipitated and were no longer dissolved in the water, so they could be decanted and the water filtered, thus removing most of the salts). This method is expensive and requires constant chemical monitoring.

We can almost completely remove all the salts contained in water (both acidic radicals such as bicarbonates, carbonates, sulfates, chlorides, and alkaline radicals such as those of calcium, magnesium, sodium, or others) using ion exchange (with resins that exchange these radicals for H-hydrogen and OH-hydroxyl ions, the former regenerated with acids and the latter with soda). Both form H2O in place of the salts: water.

This water is called demineralized water. Its preparation is very costly, and it is mainly used in high- and medium-pressure boilers.

It is inherently corrosive (for the reason mentioned earlier regarding soft water). This water quality can also be achieved through distillation (that is, evaporating the water and then condensing it, leaving the salts concentrated in a solution that is purged; formerly, this was the only way to obtain salt-free water). (after several successive evaporations to achieve high purity).

This salt-free water is called distilled water (or, depending on the number of distillations, double-distilled water, etc.).



Currently, almost "pure" water (in which almost all salts are removed) is also obtained through filtration with a membrane (cellulose or polyamide filter) that only allows water to pass through (reverse osmosis, caused by water at relatively high pressure, in which almost pure water passes through at a certain percentage, with a percentage being discarded to maintain a maximum concentration on the salt side).

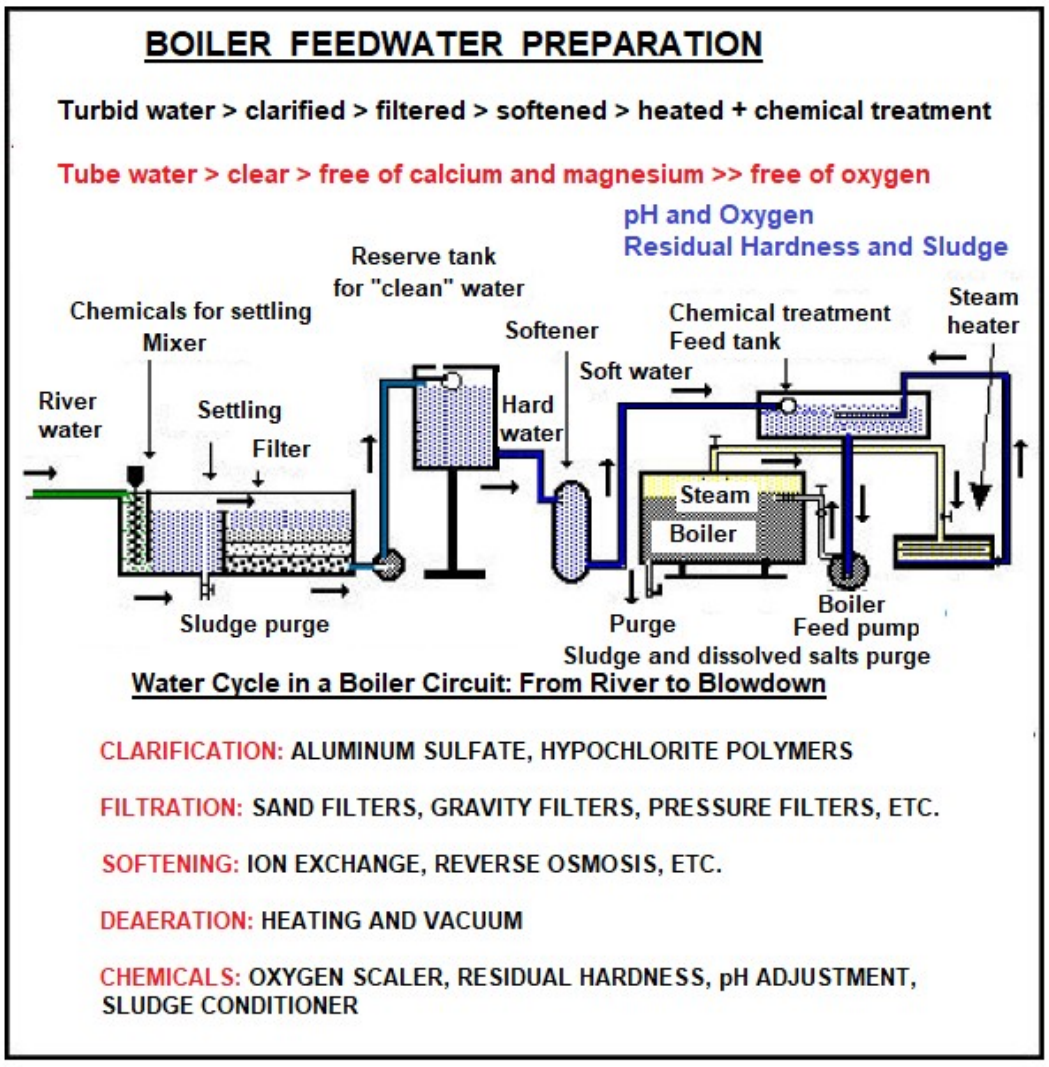
This water can be further purified by passing it through another filter and then further purified by ion exchange in a mixed bed of resins (a demineralizer with mixed resins, which are separated for regeneration).

In internal treatment, softening (removal of calcium and magnesium) is done exclusively with chemical products (which generally form sludge); like phosphates, polymers, etc., or non-sludge-forming salts such as EDTA (ethylenediaminetetraacetic acid), etc.

We see that purge plays a fundamental role in properly removing sludge (it is observed that dissolved salts decrease even with the addition of chemicals—due to precipitation—but because of the amount of sludge, it is necessary to keep the water "clear" with bottom purge).

Continuous purge removes the dissolved salts that accumulate as steam (pure water) escapes, leaving the salts behind.

Gases should be treated in the same way as rainwater.



Even if we use pure water, we must perform internal chemical treatment; otherwise, we will have corrosion problems, since pure water is corrosive (it tends to dissolve the iron that makes up the boiler).

We must never forget about silica (SiO_2, not in the form of sand, but as a soluble salt or in colloidal form; it can be removed in some of the treatments mentioned above, but not in sodium cycle softening). In boiler water, it can form very hard, insulating scale (almost impossible to remove once established), or it can be carried over in the steam, causing very serious problems in medium- and high-pressure boilers, such as deposits in the turbines (very hard scale on the steam turbine blades, causing low efficiency, severe vibrations, etc.) or in the steam superheaters (causing scale that isolates the tube from the steam, leading to tube burnout).

The higher the working pressure, the easier it is for silica to be carried away (since it tends to vaporize along with the water vapor).

WELL WATER:

This water generally contains few gases (though not always), but a very high concentration of salts—"hardness"—(generally free of suspended solids, sometimes sand).

It is very tempting for use in boilers, as it seems to be "free" and does not require the same treatment as river water for purification.

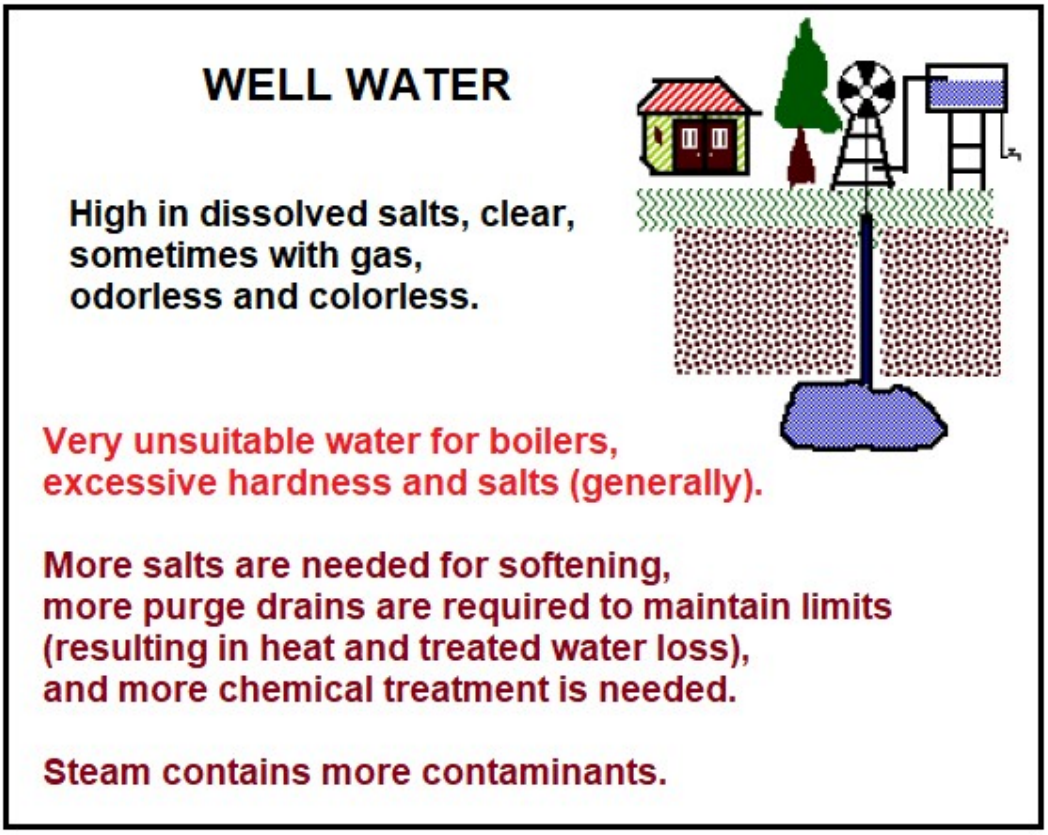
However, its use is generally inconvenient due to the cost of chemical treatment, because of the high salt content, which necessitates very high purge rates, large consumption of chemicals, and often problems with steam quality (causing "carryover" and CO_2, a highly corrosive element in the condensate).

We can say that well water varies depending on the area and depth of the well. Generally, in Uruguay, wells further south and east have high salinity (both temporary and permanent hardness), while wells north of the Río Negro and to the west have lower salinity (lower permanent hardness and salt content in general).

The high total alkalinity (calcium, magnesium, and sodium bicarbonates), responsible for temporary hardness, is due to the changes in its composition upon entering the boiler caused by heat.

This alters the composition, breaking down soluble bicarbonates into insoluble carbonates (calcium and magnesium), and in turn, the carbonates, which are totally or partially soluble, into their corresponding hydroxides.

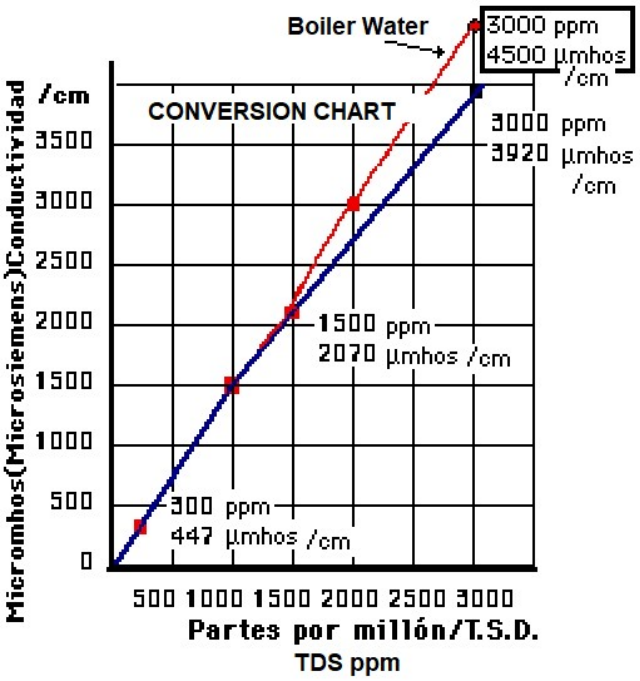
Sodium bicarbonate is soluble, while calcium and magnesium bicarbonates are less so, with the latter preferentially transforming into scale and sludge. This means that this type of water generally produces rapid scaling in boiler tubes if not properly treated.


WELL WATER
High in dissolved salts, clear,
sometimes with gas,
odorless and colorless.
Very unsuitable water for boilers,
excessive hardness and salts (generally).
More salts are needed for softening,
more purge drains are required to maintain limits
(resulting in heat and treated water loss),
and more chemical treatment is needed.
Steam contains more contaminants.

The presence of silica (SiO2) in salt or colloidal form in well water is one of the problems associated with its use. As higher steam pressure boilers are used, silica carryover can negatively impact the operation of superheated steam turbines. This silica deposits reduce turbine efficiency and can cause imbalances that may mechanically damage the turbine through vibrations. Furthermore, this deposited silica is very difficult to remove from the turbine runner blades.

Even in low-pressure boilers, the maximum silica limit in boiler water must be respected. Boilers scaled with silica salts (which are very hard and insulating, and can lead to boiler failure due to insufficient heat transfer and cooling) are very difficult to remove, whether by mechanical or chemical means. (In some cases, replacing the tubes has proven preferable to cleaning the boiler.)

GRAPH INDICATING THE RELATIONSHIP BETWEEN CONDUCTIVITY AND TOTAL DISSOLVED SALT CONTENT (TDS) OF AVERAGE NATURAL WATER AND A SUITABLE THEORETICAL CURVE FOR LOW-PRESSURE BOILER WATER AND COOLING TOWERS



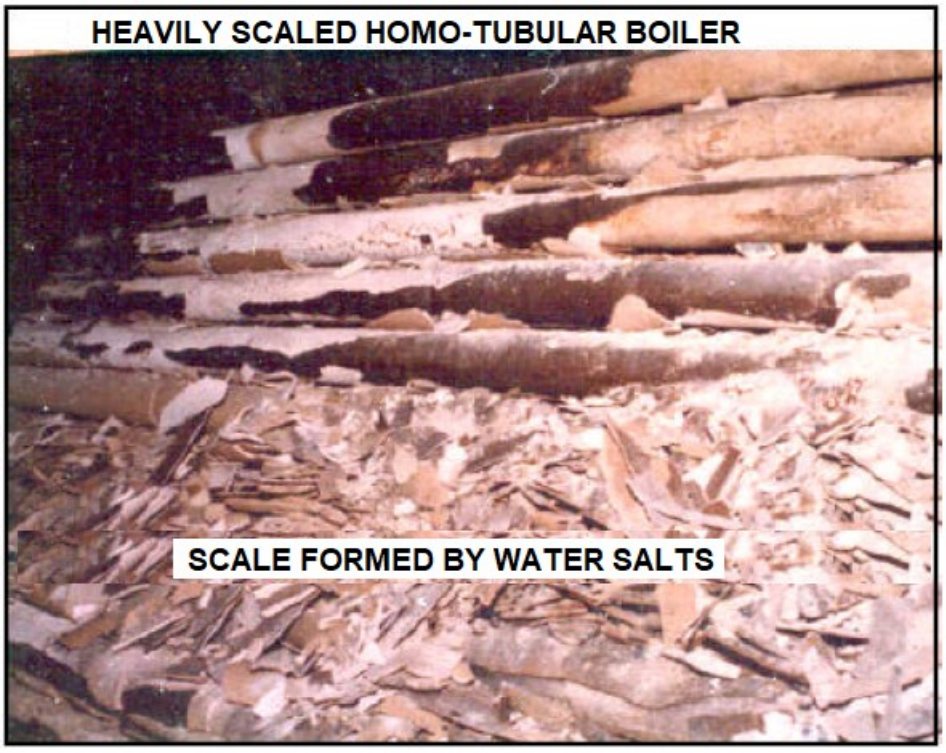
Problems Caused by Chemical Water Treatment:

Among the problems associated with water treatment, the most important is establishing the appropriate values for the analyzed parameters (alkalinity, Total Dissolved Salts - TDS, pH, phosphates, sulfites, chlorides, etc.). Even with the same boilers, pressures, and water quality, there can be differences in how steam is used:

A plant with high and rapid steam consumption tends to "carry over" the boiler water more easily. Therefore, parameters related to carryover must be lowered (alkalinity, hydroxide, pH, Total Dissolved and Suspended Solids, cycles of concentration, etc.).

In many cases, products that are "good" for eliminating a problem are added, but these same products can cause serious material damage or harm to health. (A boiler treatment takes years to properly evaluate, so be very cautious with changes and "miracle products").

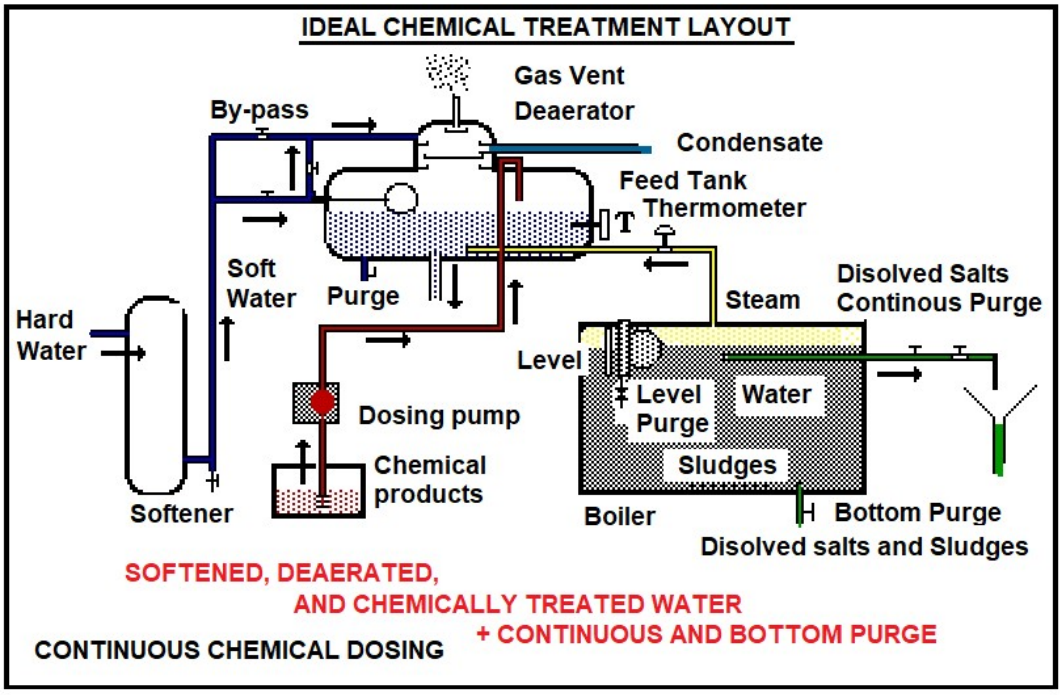
As a fundamental step, it is advisable to drain and open the boilers every 6 months, hose them down with pressurized water, and assess their condition (there is no better way; chemical analyses are relatively reliable).



Purges and how they are performed play a crucial role, because if they are not done in the correct quantity and manner, no matter how good the products used may be, the boiler or the process will be affected.

It is important to know not only which chemical products are necessary, but also how they will be used, their quantities, and the arrangement of auxiliary equipment for the treatment (water softener, dosing pumps, etc.). Scale buildup in fire-tube boilers can only be cleaned by chemical means (chemical cleaning with inhibited acids).

This process is generally divided into three parts: an alkaline preparation boil under pressure, a stage with inhibited acid (to prevent iron attack) at a specific temperature, and a third stage with an alkaline boil to neutralize the acid and with chemicals to passivate the material (restoring a protective layer to the surface attacked by the acid).



This entire process requires significant chemical and practical knowledge, as improper cleaning can damage the boiler or cause an accident. Water-tube boilers are cleaned chemically, but they can also be cleaned mechanically (with brushes, hydraulic, pneumatic, or electric turbines) since the inside of the tubes is accessible.

However, proper chemical cleaning is generally recommended. Afterward, a follow-up cleaning is necessary. "Sweeping" of scale and sludge from the entire interior of the boilers with a strong "hosing" and manual removal of fallen scale.

An ideal treatment is one that prevents corrosion, does not form scale or sludge, prevents boiler water carryover into the steam, and is economically viable.

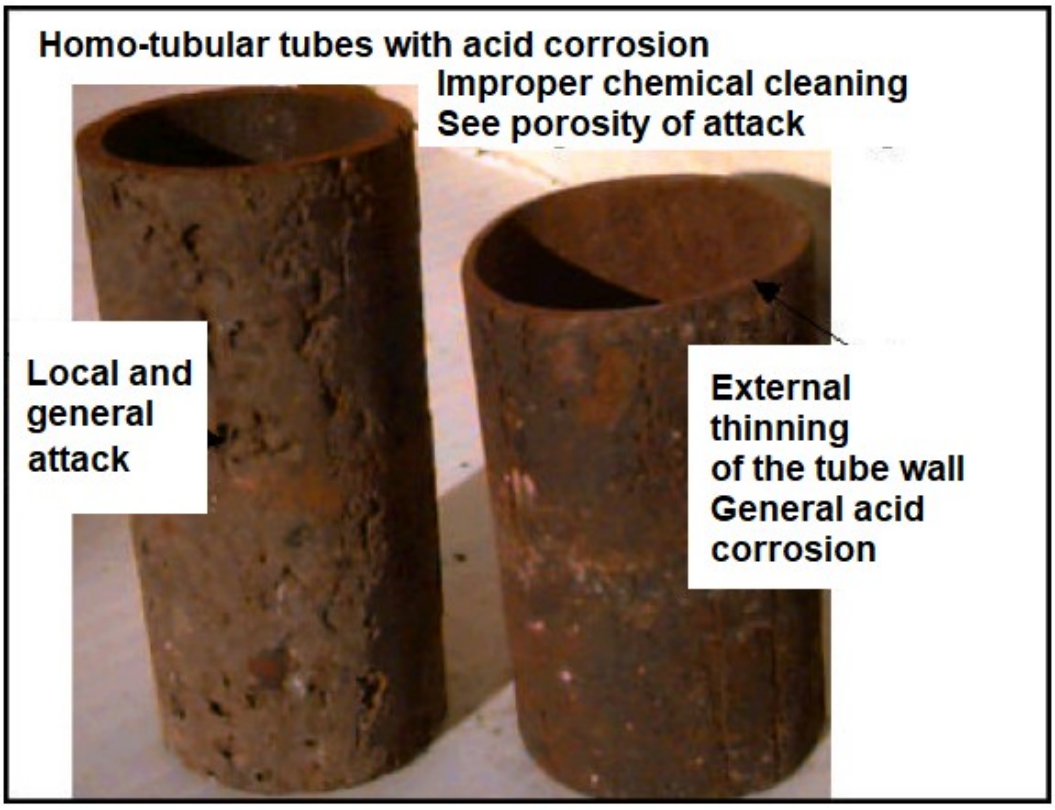
Removing all salts from the water (distilled or demineralized) would be ideal, but the cost is very high and control is quite difficult (corrosion must be controlled).

There can be problems with silica (SiO_2) if it is not removed properly, as this increases concentration cycles, can cause scaling, or lead to carryover.

Chemical treatment may be seen as a "cost," but it is actually an investment, since a boiler that does not receive proper chemical treatment is a boiler that will eventually have a problem that will not only result in the cost of repairing the boiler, but also in the cost of lost production (lost profits).

But even more importantly, boilers with inadequate chemical water treatment are generally more prone to serious accidents, ranging from a simple pipe leak to a complete explosion of the boiler casing or combustion chamber (both very serious accidents).

Poor treatment quality can lead to blocked level controls, which can cause boiler destruction due to insufficient cooling as the water level drops and the burner fails to shut off. This results in the metal being destroyed by the heat (with a high risk of explosion).


Homo-tubular tubes with acid corrosion
Improper chemical cleaning
See porosity of attack
Local and general attack
External thinning of the tube wall
General acid corrosion

Therefore, the ideal treatment (at low pressure, not in 100% of cases) is as follows:

1- Remove calcium and magnesium before the water enters the boiler.

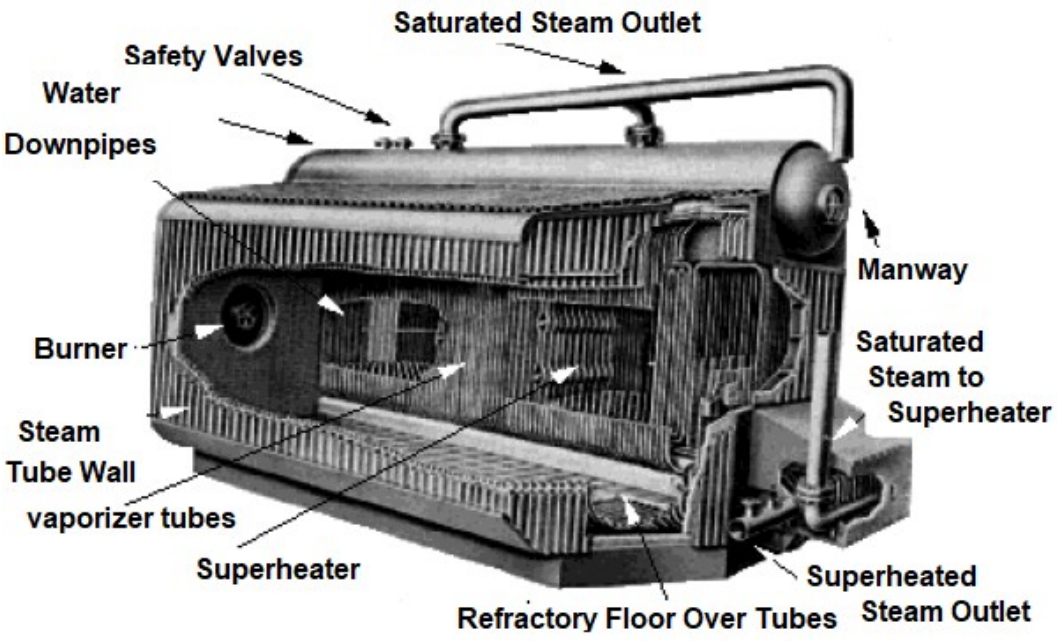
2- Remove gases (primarily oxygen). When a deaerator is not available, heat the water as close to 100°C (212°C) as possible (therefore, the feed tank must be 4 to 5 meters above the feed pump to prevent cavitation and allow for steam heating).

3- Internal treatment with continuous dosing to remove residual oxygen, maintain a level of products that eliminates residual hardness, and regulate the pH (low pH = corrosive acid, very high pH = corrosive due to instability of the protective oxide layer and water carryover in the steam).

4. An analytical system for monitoring (shift, daily, weekly, etc.; softener testing per shift = hardness), implemented on-site by the boiler operator.

5. A continuous purge system (including level checks every 4 hours), maintaining values within their maximum permissible limits. (It is important to be able to measure the flow rate per minute of the continuous purge, with a measurement point located downstream of the heat recovery unit for flash steam removal).

6. Recover as much condensate as possible; it is generally pure water. (Possible contamination in the condensate should be monitored through analysis.)



Modern FM Type Water-Tube Boiler